EVALUATION OF THERMAL DEGRADATION IN GRAPHITE FIBER-EPOXY LAMINATES: CORRELATION USING ULTRASONIC SPECTROSCOPY AND INTERLAMINAR FRACTURE TOUGHNESS TESTS

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ABSTRACT

In certain fire situations, a structural component made from a polymer matrix composite (PMC) may be exposed to excessive thermal loads that degrade the matrix and the fiber/matrix interface. In this paper, we report the results of a study to assess the utility of ultrasonic spectroscopy as means of assessing the residual characteristics of PMCs exposed to excessive thermal loads. In addition, we discuss the results of interlaminar fracture toughness tests as a function of exposure temperature using double cantilever beam specimens. Long term – low intensity thermal loads induce an attenuation in the power spectra that occurs primarily by eroding the highest frequencies first and progressing to the lower frequencies as the degradation progresses. These long-term loads cause a large reduction in the measured fracture toughness.   Short term – high intensity loads induce substantial degradation of the composite. However, the fracture toughness of a given sample increases prior to regions where gross thermal-induced delamination occurs. The amplitude of the power spectra was also observed to increase sharply prior to its complete attenuation in areas of gross delamination. Investigation of the fracture surface by scanning electron microscopy(SEM) suggests that the degradation is not limited to the fiber/resin interface but occurs within the epoxy matrix as well.

KEYWORDS: Thermal Degradation, Ultrasonic Spectroscopy, Graphite Fiber Composite, Interlaminar Fracture Toughness

INTRODUCTION

Polymer matrix composites (PMCs) are structural materials used in many engineering applications including commercial aircraft, marine vessels, offshore oil platforms, and automobiles. Over recent years, a safety concern has been raised regarding the use of these materials in situations where potential fire could erupt due to their general susceptibility degrade, decompose, or even combust in certain conditions.

In certain fire situations, a structural or load-bearing component made from a PMC may be exposed to excessive thermal loads that may only char the surface of the material and thermally degrade the matrix below the surface. This thermal degradation may, in turn, dramatically affect the mechanical integrity long before pyrolysis of the matrix occurs. Also, in controlled fire situations, structural or load-bearing components may be exposed to excessive temperatures for short periods of time and show little or no apparent signs of degradation. In these situations, questions arise with regard to what the residual strength is and what non-destructive methods are available today to assess its residual strength. Because of their inherent heterogeneity, damage in composites occurs more readily compared to homogeneous materials. This is especially true in crosslinked polymer matrices which are relatively brittle compared to thermoplastics and metals. In this paper, we report the results of a study to assess the utility of ultrasonic spectroscopy as a means of assessing the residual characteristics of PMCs exposed to excessive thermal loads.

The use of ultrasound in non-destructive testing has become commonplace in many industries. Currently, ultrasonic B-scans and C-scans are routinely used to image defects in metal, ceramic, and polymeric materials. These methods are useful for mapping larger defects and cracks but are limited in the minimum size which can be detected.

However, technological advancements over the recent years in ultrasonic, data acquisition, and processing equipment have enabled the implementation of a number refined spectroscopic methods to investigate the microstructural characteristics of materials. Recently, several studies have reported results from heterogeneity induced ultrasonic attenuation . These methods have been successfully applied to porous metals (Alder, 1986), to polymers and liquid crystalline systems (Matsushige, 1985), to porous epoxy (Hughes, 1987), and to polymer latex emulsions (Verdier and Piau, 1997) and colloid suspensions (Matsuoka, 1997).

O'Donnell et. al. (1978) explored the existence of general relationships between ultrasonic attenuation and phase velocity (i.e., dispersion). In their study, they presented local forms of the general Kramer's-Kronig relationships under the assumptions that the are sufficiently small and do not change rapidly over the frequency range of interest. The local forms relate the attenuation to phase velocity as described over a definite (as opposed to indefinite range) which is of great practical use for application with ultrasonic transducers with a finite range of frequencies. They then illustrated the suitability of these relationships on hemoglobin solutions.

By the mid to late 80's, characteristic power spectra for a number of semi-crystalline and amorphous polymers had been measured including PE, PTFE, PMMA, and PC (Matsushige, 1985). Comparative studies have also been done to assess changes in the power spectra resulting from controlled heterogeneities including 0.3 -0.5 mm bubbles in PC, and changes resulting from nematic to isotropic phase transitions in liquid crystalline systems (Matsushige, 1985). These studies were conducted in the 5 MHz range.

In 1986, average pore size down to 100 µm was detected porous aluminum alloy casting (Alder, 1986). These studies were conducted over frequencies ranging between 1 and 20 MHz. Similar studies were conducted on porous epoxy (Hughes, 1987) in using a similar range of frequencies reported by Alder (1986). However, due to the slower wave speed in the epoxy media, attenuation due to scattering could be detected from pores of average size less than 60 µm. Most recently, these methods have been applied to characterize the particle size in latex emulsions (Verdier and Piau, 1997) and colloid suspensions.

In this paper, we investigate the potential of this method to detect mechanical degradation of PMCs exposed to excessive thermal loads. Specifically, we are interested in mechanical degradation that occurs at or near the fiber-resin interface in graphite reinforced epoxy based thermoset composite laminates. Herein, we report results from an investigation whereby unidirectional laminates were exposed to excessive thermal loads predominately along the fiber with the sole purpose to preferentially thermally degrade the polymer near at or near this interface. Ultrasonic excess attenuation from these laminates are then correlated to a standard interlaminar fracture toughness tests to characterize the residual behavior of the composites after exposure to the excessive thermal loads. We categorize the thermal loads as short term-high intensity loads and long term-low intensity loads where the exposure temperature is significantly less for the latter.

EXPERIMENTAL

Laminate Fabrication

The laminates for the long term exposure study were fabricated from a commercially available prepreg, R922 provided by Hexcell Corporation. The prepreg is made with a G30-500 graphite fiber and an amine cured epoxy-based matrix. Unidirectional panels of 30 plies total thickness were fabricated and cured in accordance with the manufacturer's recommendations. The panels were fabricated in a hand lay-up fashion with a 0.7 mm Teflon spacer inserted midway through the lay-up sequence along one edge of the panel. The panels were then compression molded with a final cure stage of 2.5 hours at 176^0 C and 840 KPa pressure. Double cantilever beam (DCB) tests specimens were then machined from each panel to a total length of 20 cm and a width of 2.5 cm. The notch from produced from the Teflon spacer measured approximately 12 mm. The laminates for the short term-high intensity testing were fabricated from a 3501-6 Hexcel prepreg consisting of a IM6 graphite fiber and a B staged epoxy resin. These panels were fabricated according to the manufacturer's cure schedule in United McGill autoclave using a standard vacuum bag/hand lay-up technique. The 30 ply laminates utilized an aluminum foil spacer midway through the laminate. DCB specimens were constructed as described above.

 Heat Exposure

 Thermogravimetric analyses were conducted on samples of the laminates to determine an approximate decomposition temperature. A 15 mg sample was heated at a rate of 10^0 C /min. This test indicated the onset of degradation for this material to be in the range of $310^0 – 330^0$ C. Based on these results, we define a short term-high intensity thermal load as exposure to

temperatures above the onset of degradation.

After the DCB specimens were ultrasonically scanned to obtain the average power spectra, an edge containing fiber ends (either the notch side or the opposing side) was polished. Thermocouples were then placed at the polished end, the opposing end and at different points along the length of each specimen. The specimens were then wrapped with glass wool to act as a thermal insulation and the polished edge was exposed to a heat source for a pre-specified length of time.

The long term-low intensity studies involved submerging the polished tip of the specimens into a 12 mm deep silicone oil bath. The oil bath was maintained at a temperature of 205^0 C and the specimens were exposed for a period of 28 days. The steady-state temperature measured at the mid-point averaged 130^0 C and the temperature at the opposing end averaged approximately 90^0 C. For these experiments, the notched ends were submerged into the oil bath.

The second type of heat exposure is similar the first case except that sand at a temperature of 350, 400, or 450^0 C was used. The edges of the DCB specimens were submerged into the heated sand for a period of 90 minutes. The ends opposite the notched ends were polished and directly exposed to the heat source in this set of experiments. This was necessary since severe decomposition of the composite prohibited further preparation of the DCB specimens (i.e., application of the hinges) if the notched ends were exposed.

Ultrasonic Spectroscopy

Selected DCB specimens were submerged in water and scanned in a backscatter (pulse/echo) mode with a Panametrics Inc. 20 MHz focused transducer. The transducer used has a 3 mm diameter element and a focal point 19 mm from its face. A Panametrics Model 5601A/TT pulser/receiver was used to drive the transducer. The signal from the pulser/receiver was digitized at a rate of 1 GHz with a Sonix STR81G PC based digitizer. A schematic of the acoustic equipment is shown in Figure 1.
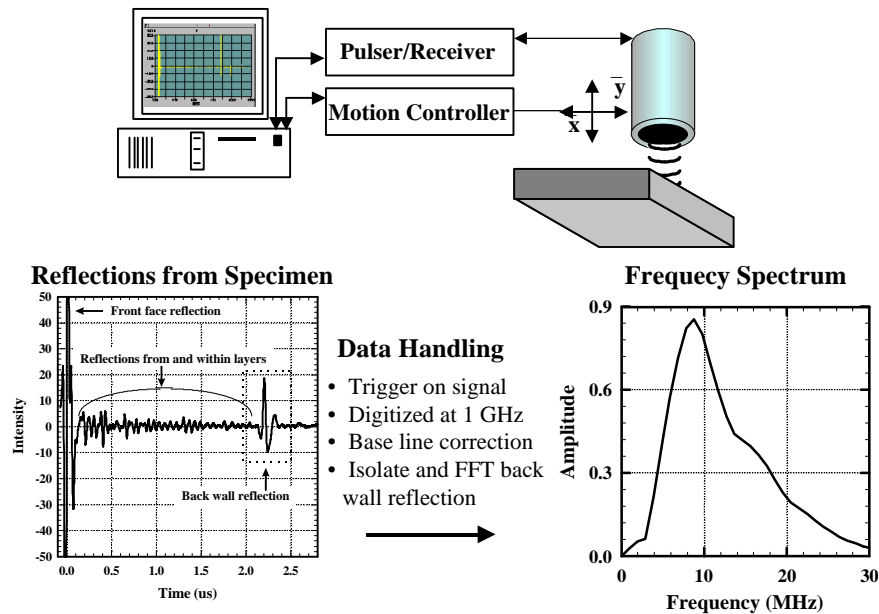

Figure 1: Schematic of the Acoustic Spectroscopy Setup

Panametrics Inc. Multiscan software was used to set the trigger threshold and gate the echoes returning from the sample. The software controls two stepper motors that move the transducer in the X and Y directions via Panametrics P1399 position match generator and MEI motion controller. Before scanning, the specimens were brushed while submerged to remove surface bubbles. Three A-scans were collected and averaged every 0.25 mm along the length of the sample and digitally stored as a B-scan. B-scans were collected every 2.5 mm along the width of the sample. The B-scans were collected to form a three-dimensional data array for each DCB specimen. The 3D array can be separated into A-scans at selected points in the specimen, B-scans along the length or width of the specimen, and C-scans to map specific depths across the entire sample.

Analysis of the specimen was conducted by isolating the back wall reflection from the A-scan, correcting its baseline, and transforming it into the frequency domain. The back wall reflection was chosen for analysis because it represents sound that had traveled through the specimen twice and would be most sensitive to changes in the sample. This process is illustrated in the bottom portion of figure 1.

The standard technique of ultrasonic spectroscopy (figure 1) utilizes two types of time domain traces for measurement of the attenuation coefficient and dispersion. The first is a reference trace typically acquired from a water-only-path. Subsequently, the second is the trace obtained from the specimen. In our case, we utilize the specimen traces from samples before exposure as the reference traces and traces from the heat exposed samples to calculate the attenuation. For the long term – low intensity exposed specimens, the attenuation was calculated using two traces. The reference was the averaged frequency spectra along the length of the unaged specimen. However, for the short term – high intensity specimens, the amplitudes of the frequency spectra were directly compared.

Mode I energy release rate measurement (G_{1c})

The DCB test specimens were prepared for testing by first adhering hinges to the opposing faces near the end of the notch tip for gripping, and coating the sides of the specimens with a white paint. The test specimens were carefully loaded to pre-crack them before the actual testing started. During this initial loading, any debris bridging the notch surfaces was cut away with a razor blade. The Mode I tests were conducted at a crosshead speed of 2 mm/min. Crack lengths were measured optically during the testing and verified/corrected after inspection of the fracture surfaces after the testing was complete.

The energy release rates were determined using the compliance method (Williams and Kinloch, 1989) using measured values of critical load for that crack length together with the specimen compliance at the specified crack lengths. In this approach, the measured compliance is used to calculate the energy release rates using Equation 1:

$$G_{IC} = \frac{P^2}{2b}\frac{\partial C}{\partial a}$$

(1)

where G_{IC} is the energy release rate (fracture energy), P is the applied load, C is the specimen compliance, a is the crack length, and b is the specimen width. Figure 2 is a plot of the measured compliance versus crack length curve for the short term – high intensity DCB test specimens. The curve fit for each specimen is a third order polynomial with a correlation coefficient ≥ 0.990.
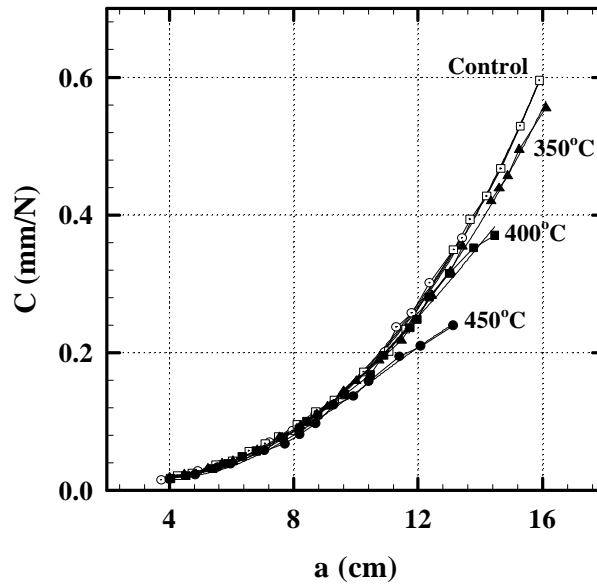
Figure 2: Plot of Measured Compliance vs. Crack Length for Short Term Specimen

DISCUSSION

Each DCB specimen was ultrasonically scanned as detailed in the experimental in Section 2. Note that although a 20 MHz transducer was used the peak frequency from the reflected energy occurred at approximately 7 MHz. This is shown typically for a specimen in Figure 3. Note that the power spectra was windowed from the back reflection off the back wall of the specimen to maximize response from the attenuation from the sample. If the sample were removed and the time trace was analyzed without the DCB specimen, the center of energy would be closer to the 20 MHz transducer rating. This implies that the unidirectional panel is adsorbing a significant amount of the higher frequency sound.

A series of DCB test specimens were then exposed to a high temperature heat source. Only one end of the specimen was exposed to the heat source to promote a steady-state gradient of temperature along the length of the specimen. Consequently, it was anticipated that a single specimen exposed in this fashion would contain a similar gradient of resin and fiber-resin interfacial degradation that could be correlated with ultrasonic and fracture toughness measurements.

DCB specimens were exposed to two different conditions (see Section 2). One series of specimens were exposed at one end to a temperature of 205^0 C for a period of 28 days and a second set was exposed to temperatures $\geq 350^0$ C for a period of 60 minutes (short term-high intensity).

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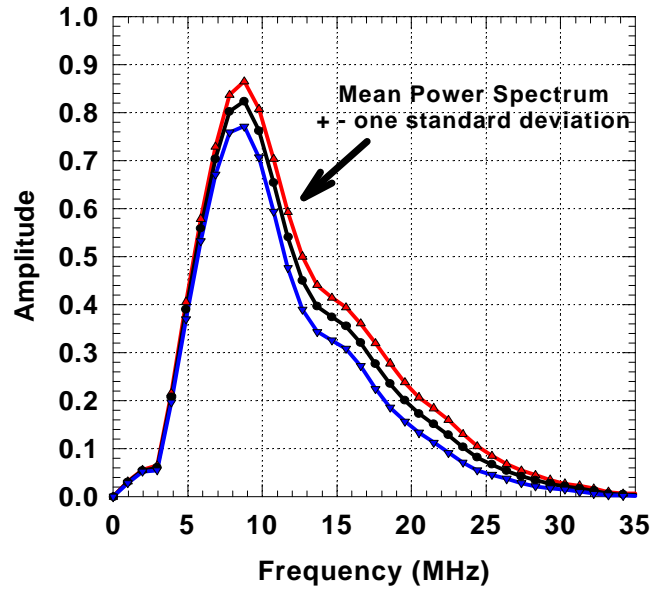
Figure 3: Power Spectrum of Untreated Sample

Long term- low intensity exposure

After exposure, the DCB specimens were again ultrasonically scanned as described in Section 2. However, in these scans the power spectra were not averaged along the length of the specimen, as was the case for the sample before exposure. Instead individual power spectra were recorded and plotted at selected positions along the length of the exposed specimens. These spectra are shown typically for the test specimens exposed to 205^0 C for 28 days in Figure 4. The plots in Figure 4 are labeled with numbers that denote the measurement distance away from the heat source. Figure 4 shows that there is a clear reduction in the power spectra that becomes more pronounced as measurements are taken nearer the heat source. This, of course, indicates that additional attenuation occurs in the composite as a consequence of the heat exposure. The change in amplitude is quite pronounced and much larger than one standard deviation obtained from an unexposed sample.
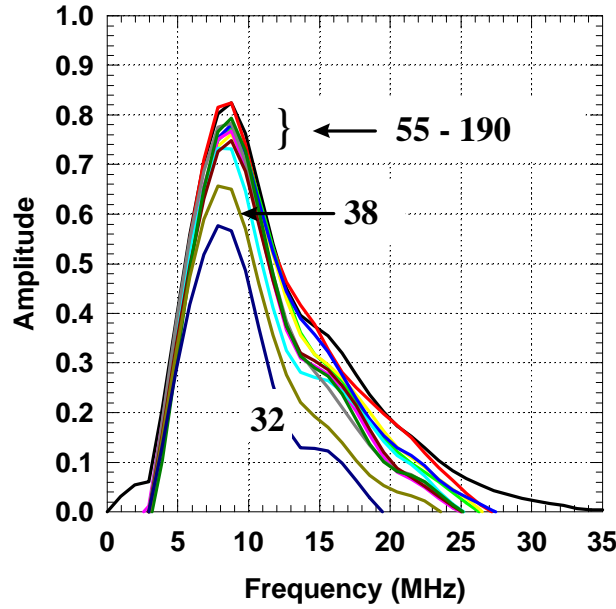
Figure 4: Power Spectra for the DCB Specimen Exposed to 205^{0} C Heat Source.

The attenuation, A(*f*), of ultrasonic energy due to the heat treatment on the DCB specimen can be calculated by:

$$A(f) = A_w - \ln\left(\frac{P}{P_o}\right) \tag{2}$$

where A_w is the attenuation coefficient of water, P_o is the power spectrum intensity before exposure (Figure 3) and P is the intensity after exposure (Figure 4). The attenuation spectra for the sample heat aged at 205^{0} C are presented in Figure 5.

It is interesting to note from Figure 5 that total attenuation occurs over the entire length of the sample at frequencies greater than approximately 20 MHz. However, as measurements are taken closer to the heat source, significantly more acoustic energy is attenuated at lower frequencies.   The amount of attenuation continues to increase to the point where, at 32 mm away from the heat source, nearly 40% of the energy is attenuated at 5 MHz, and all acoustic energy is attenuated above 13 MHz.
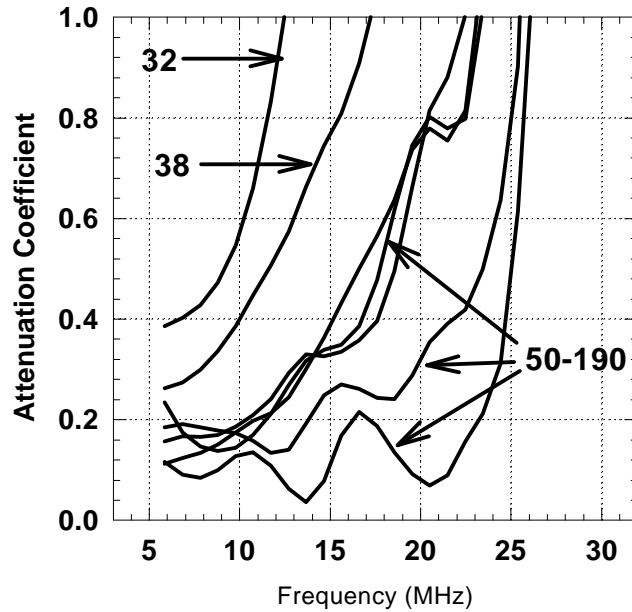
Figure 5 : Ultrasonic Attenuation for Sample Heat Aged at 205 ^{0} C for 28 days

Mode I interlaminar fracture toughness tests were performed to obtain critical energy release rates(G_{IC}) using the DCB specimen to evaluate if any degradation in the resin or resin/fiber interface occurred as a consequence of the heat loading. Under normal conditions, the energy critical energy release rate becomes independent of crack length and is ascribed the value of G_{IC}. As a result, a typical test on DCB specimens usually reaches a steady state condition corresponding to the G_{IC} value. However, if the fracture energy changes along the specimen's length, as we might expect from our heat treated samples, then a steady state value will not be reached. Hence, a large amount of information can be obtained from a single specimen if the thermal gradient is known.

Figure 6 shows the G_{IC} results for a control (unexposed) and one exposed to the heat treatment. Note first that control specimen produced a G_{1c} value of 260 J/m^2. This value is in the range of that reported by the manufacturer (Lee, 1998) and differences might be attributed to variations in fiber volume. More importantly, Figure 6 shows that the fracture energy measured on the heat-treated samples were significantly reduced by approximately 50% to levels ranging between 120 - 160 J/m^2. Also, the fracture energies on the heat-treated sample are at their lowest value nearest the heat source and increase gradually as measurements are made further away from the heat source. The experimental data clearly show a significant decrease in fracture toughness after long term-low intensity exposures.
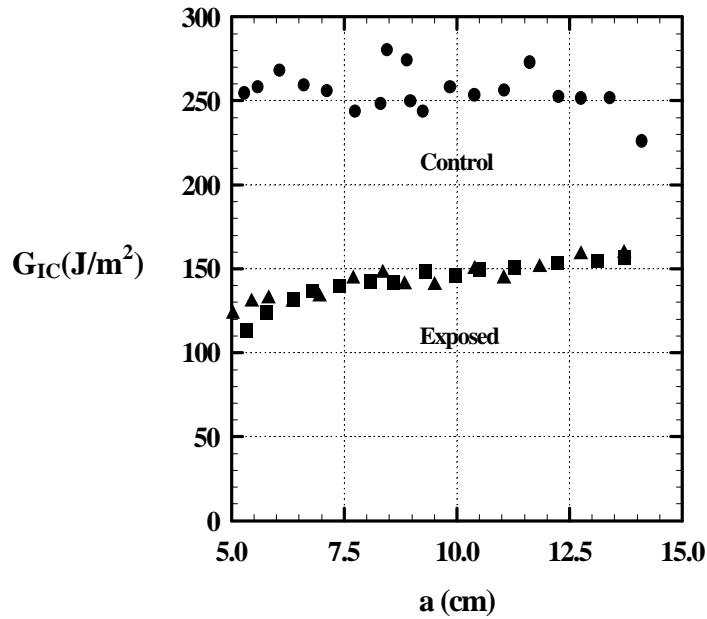
Figure 6: G_{1C} Fracture Measurements on DCB Control and Heat-treated (205^0 C for 28 days).

Short term –high intensity exposure

The ultrasound data was collected in a similar manner to the long term exposure specimens. For the short term specimens, the strongest signal occurred at the end of pulse echo waveform which is the reflection from the back wall of the specimen. This signal was used for correlation with the fracture toughness tests as it represents the composite as a whole because the wave travels through the specimen thickness twice. A slight variation exists in the amplitude of the signal as a function of sample length due to small defects in the sample. The composite panels, however, are very high quality as indicated by ultrasound C scans prior to testing. For analysis, the reflection from the back wall was isolated, its baseline corrected, and then transformed into the frequency domain via fast Fourier transform. For ultrasound discussion, we will focus on the 450^0 C specimen. Figure 7 shows the temperature profile recorded as a function of sample distance. For the steady state data, temperature can be correlated to sample length using a quadratic function.

G$_{IC}$ values were also measured for the short term-high intensity tests as described in the experimental section. The G$_{IC}$ values for the three temperatures tested are shown as a function of distance from the heated end in figure 8. All three samples follow a similar trend showing an increase in fracture toughness as one approaches the heated end. The maximum increase in fracture toughness is approximately 41%. The microscopic mechanism for the increased toughness is mainly fiber bridging and gapping. Investigation of the fracture surface by scanning electron microscopy indicated that less resin was present at higher exposure temperatures and failure occurred in the resin between lamina.

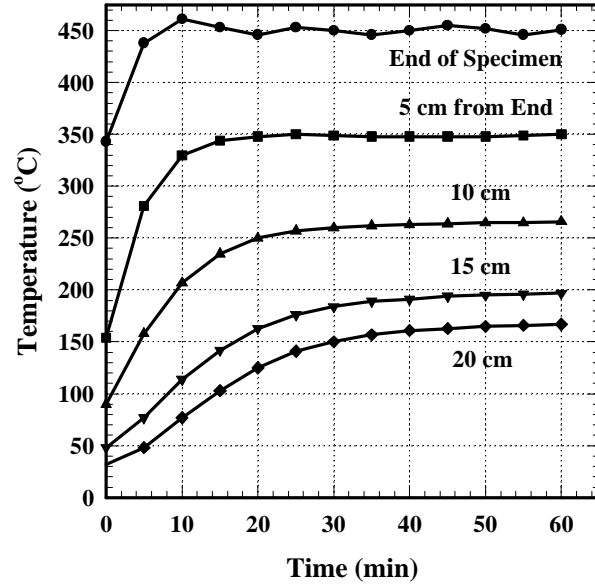The increase in fracture toughness recorded can be attributed to higher loads during the test.

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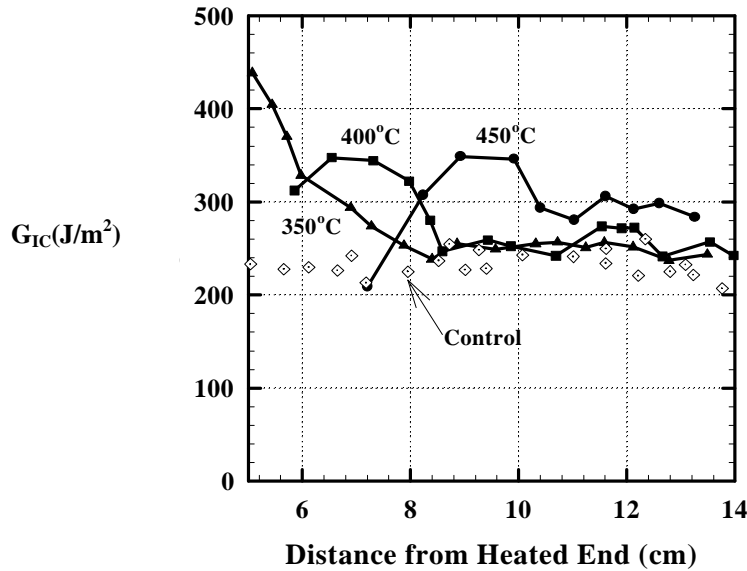Figure 7. Temperature Profile for 450^0 C Specimen.

Figure 8: Energy Release Rate for Short term-High intensity Samples

Calculation of the energy release rate is dependent on the P^2 term in equation 1. For a standard specimen such as an unexposed one, the load required to propagate a crack decreases as crack length increases. However, for the short term samples, the loads began increasing at a certain point along the specimen depending on the exposure temperature. The material has undergone a significant change after heat exposure as the material stiffness also becomes greater,

i.e. the compliance is lower as shown in figure 2.

Figure 9 shows the correlation of the fracture toughness with ultrasound data. The amplitude at 8.8 MHz increases with heat treatment indicating transformation of the material. Prior to the largest increase in fracture toughness, the amplitude increases and then drops off sharply. It should be noted that the fracture toughness is also greater compared to the original or untreated specimen as shown previously in figure 8.
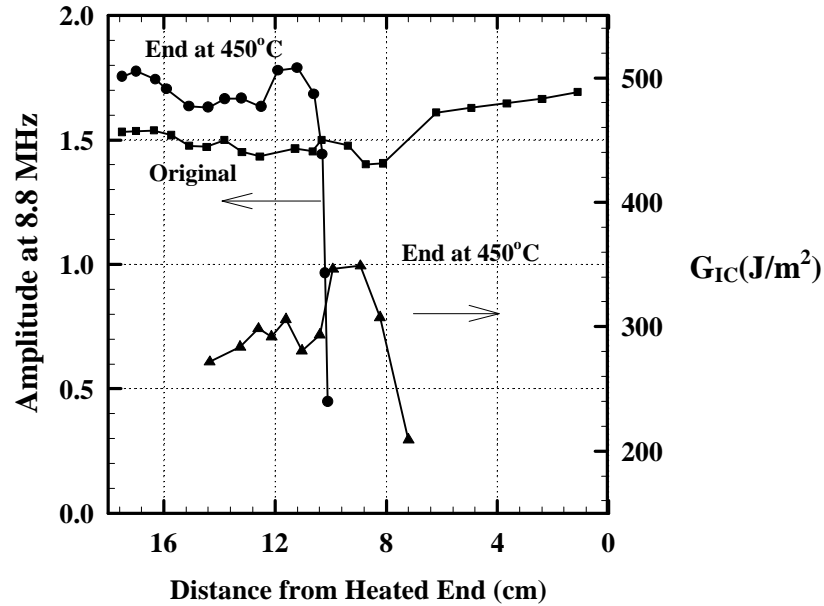

Figure 9. Correlation of Amplitude and G_{IC} with Specimen Distance

Based on the known temperature profile of the specimen, the G_{IC} values and ultrasound results can be easily correlated simply by associating a temperature with a specimen distance through a quadratic equation. For samples with different temperature profiles as a function of distance, this results in a collapse of the profiles as shown in Figure 10 for the different graphite-epoxy composite samples. These results show that severe degradation occurs at 250^0 C as marked by a sharp drop in waveform amplitude independent of temperature profile.
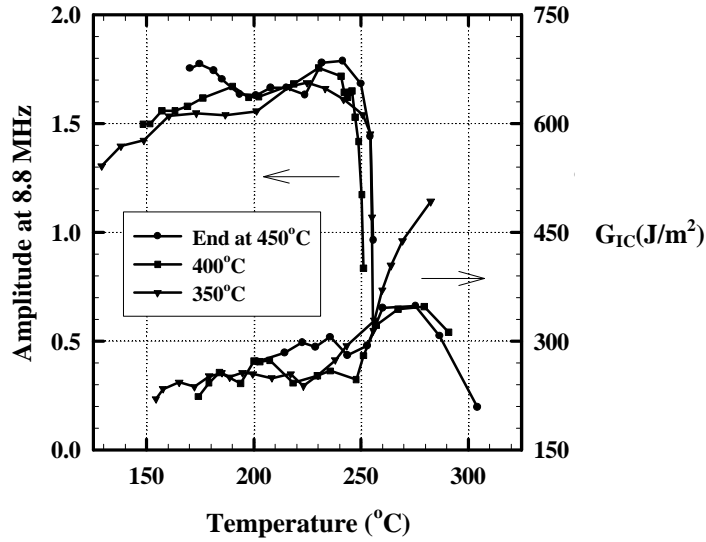
Figure 10. Correlation of G_{IC} and Amplitude with Exposure Temperature

CONCLUSIONS

This study has shown that the attenuation measured in the power spectra of ultrasonic energy correlates with degradation in composite performance on graphite fiber epoxy matrix composites exposed to thermal degradation. Attenuation in the power spectra occurs primarily by eroding the highest frequencies first and progressing to the lower frequencies as the degradation progresses. The range of frequencies we observed most sensitive are between 5-25 MHz. However, at the lower frequencies (i.e., < 5 MHz) visual degradation is also evident. Hence, if this method is to be considered practical as a non-destructive method for evaluation thermal degradation, frequencies greater that 5 are suggested.

Mode I fracture toughness tests also correlated with thermal exposure showing lower values nearer the heat source for long term-low intensity exposures. For short term-high intensity exposures, the behavior was altogether different as G_{IC} values increased as the heat source was approached. Excellent correlation was obtained between G_{IC} measurements and ultrasound back wall reflection amplitude as the fracture toughness increased and the amplitude declined sharply near $250^{0}C$.

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ACKNOWLEDGEMENTS

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